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Reaction of $KIn(CH_2CMe_3)_3H$ with Chlorodiphenylphosphine

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Summary: The reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ in pentane or benzene produces significant yields of two indium−phosphorus compounds, $(Me_3CCH_2)_2InPPh_2$ and $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$. This unexpected adduct incorporates a neopentyl group that was originally a substituent on the indium reagent. The other products of the reaction are CMe_4, H_2, and KCl. The formation of all products is explained by a set of experimentally verified reactions.

Introduction

The original and simplest route to compounds of the type $R_2InPR'_2$ involves the use of the hydrocarbon elimination reaction[1−3] between InR_3 and HPR'_2. Even

$$InR_3 + HPR'_2 \xrightarrow[\text{reaction}]{\text{hydrocarbon elimination}} R_2InPR'_2 + RH \quad (1)$$

though the metathetical reaction[4] between InR_2Cl and $LiPR'_2$ and the Me_3SiCl elimination reaction[5] between InR_2Cl and $(Me_3Si)PR'_2$ have also been exceedingly useful and productive reactions to prepare $R_2InPR'_2$, the latter reactions require the synthesis of more starting materials than are needed for the simple hydrocarbon elimination reaction. Therefore, a goal of our research has been to develop a procedure for the preparation of $R_2InPR'_2$ that would take advantage of the simplicity of the hydrocarbon elimination reaction but that would not require the prior synthesis and handling of HPR'_2. Ideally, the secondary phosphine should be formed in-situ and then be consumed by reaction with the organoindium compound. This goal was realized with the synthesis of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ in high, if not quantitative, yield by reacting $KIn(CH_2CMe_3)_3H$[6] with $ClP(t\text{-}Bu)_2$ in pentane (eq 2).[7] In contrast, we have found

$$KIn(CH_2CMe_3)_3H + ClP(t\text{-}Bu)_2 \xrightarrow{\text{pentane}} (Me_3CCH_2)_2InP(t\text{-}Bu)_2 + KCl + CMe_4 \quad (2)$$

that the reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ forms a different set of products and thus involves some reactions that were not observed for the *tert*-butyl phosphine system.[7]

Results and Discussion

The reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ in either pentane or benzene produces two indium−phosphorus compounds $(Me_3CCH_2)_2InPPh_2$[2,3] and $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$, which account for approximately 85−90% of the initial indium and phosphorus. The other products that were isolated from the reaction included CMe_4, H_2, and KCl. The identity of the principal product $(Me_3CCH_2)_2InPPh_2$ was confirmed by observing that its physical properties as well as its ^1H and ^{31}P NMR spectra were identical with those for samples prepared by the elimination reaction between $In(CH_2CMe_3)_3$ with $HPPh_2$ in pentane or benzene solution.[2,3] Thus, $(Me_3CCH_2)_2InPPh_2$ has been synthesized directly from the chlorophosphine without the intermediate preparation and isolation of $HPPh_2$. The second indium−phosphorus product is $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$, an adduct of a tertiary phosphine that contains a neopentyl group that was a substituent on the initial indium reagent. The ^1H and ^{31}P NMR spectra of this adduct were identical with those of a sample prepared from a 1:1 mixture of $In(CH_2CMe_3)_3$ and

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$P(CH_2CMe_3)Ph_2$ that had been prepared independently by using the literature method.[8]

The occurrence of the reactions shown by eq 3−9 readily explains the formation of all products, is in agreement with their observed percentage yields, and is consistent with indium and phosphorus chemistry. All reactions in this sequence have been verified by independent experiments. These reactions account for the formation of $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$ and H_2, the two products that were unexpected on the basis of the reaction between $KIn(CH_2CMe_3)_3H$ with $ClP(t\text{-}Bu)_2$.[7] These two products also explain why $(Me_3CCH_2)_2InPPh_2$ and CMe_4 were not formed in equimolar amounts as required by the balanced equation for the hydrocarbon elimination reaction (eq 4). The percentage yield of $(Me_3CCH_2)_2InPPh_2$ (40.2%) was significantly higher than the yield of CMe_4 (27.0%). Thus, $(Me_3CCH_2)_2InPPh_2$ must be formed by more reactions than only the hydrocarbon elimination reaction.

Pathway for Reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$

$$2\,\{KIn(CH_2CMe_3)_3H + ClPPh_2 \longrightarrow In(CH_2CMe_3)_3 + HPPh_2 + KCl\} \quad (3)$$

$$In(CH_2CMe_3)_3 + HPPh_2 \longrightarrow (Me_3CCH_2)_2InPPh_2 + CMe_4 \quad (4)$$

$$KIn(CH_2CMe_3)_3H + HPPh_2 \longrightarrow H_2 + K[(Me_3CCH_2)_3InPPh_2] \quad (5)$$

$$K[(Me_3CCH_2)_3InPPh_2] + ClPPh_2 \longrightarrow (Me_3CCH_2)_2InPPh_2 + (Me_3CCH_2)PPh_2 + KCl \quad (6)$$

$$In(CH_2CMe_3)_3 + ClPPh_2 \longrightarrow In(CH_2CMe_3)_2Cl + (Me_3CCH_2)PPh_2 \quad (7)$$

$$K[(Me_3CCH_2)_3InPPh_2] + In(CH_2CMe_3)_2Cl \longrightarrow In(CH_2CMe_3)_3 + (Me_3CCH_2)_2InPPh_2 + KCl \quad (8)$$

$$In(CH_2CMe_3)_3 + (Me_3CCH_2)PPh_2 \longrightarrow (Me_3CCH_2)_3In{\bullet}P(CH_2CMe_3)Ph_2 \quad (9)$$

Overall Reaction as Sum of Above Steps
(Equations 6 and 7 with 8 are alternative routes to $(Me_3CCH_2)_2InPPh_2$)

$$3\,KIn(CH_2CMe_3)_3H + 3\,ClPPh_2 \xrightarrow[C_6H_6]{C_5H_{12}\text{ or}} 2\,(Me_3CCH_2)_2InPPh_2 + (Me_3CCH_2)_3In{\bullet}P(CH_2CMe_3)Ph_2 + 3\,KCl + CMe_4 + H_2 \quad (10)$$

When the original reagents $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ were combined, an insoluble solid formed. This observation suggests the presence of KCl, whereas $In(CH_2CMe_3)_3$ and $HPPh_2$ (eq 3) would be soluble in pentane and benzene and undergo the hydrocarbon elimination reaction to form $(Me_3CCH_2)_2InPPh_2$ and CMe_4 (eq 4).[2] However, since both the initial reaction (eq 3) and the elimination reaction (eq 4) are relatively slow,[2] additional reactions occur to produce $(Me_3CCH_2)_2InPPh_2$. The second route to $(Me_3CCH_2)_2InPPh_2$ must begin with the reaction between $HPPh_2$ and $KIn(CH_2CMe_3)_3H$ to form H_2, an observed but unexpected product, and $K[(Me_3CCH_2)_3InPPh_2]$ (eq 5). These observations suggest that $KIn(CH_2CMe_3)_3H$ reacts faster with $HPPh_2$ than with $ClPPh_2$. An independent experiment verified that a solution of $KIn(CH_2CMe_3)_3H$ reacted with $HPPh_2$ within minutes of mixing to form H_2 and an insoluble solid, presumably $K[(Me_3CCH_2)_3InPPh_2]$ (eq 5). An additional datum in support of the occurrence of these reactions is the observation that 96.8% of the hydridic hydrogen initially available in $KIn(CH_2CMe_3)_3H$ is accounted for by the formation of H_2 (both hydrogen atoms originate with this hydride) and CMe_4. After $K[(Me_3CCH_2)_3InPPh_2]$ has been formed, it can react with $ClPPh_2$ to form $(Me_3CCH_2)_2InPPh_2$, $P(CH_2CMe_3)Ph_2$, and KCl (eq 6), as verified by an independent experiment. Thus, $K[(Me_3CCH_2)_3InPPh_2]$ transferred a neopentyl group to $ClPPh_2$ to form $P(CH_2CMe_3)Ph_2$ rather than a PPh_2 group to form P_2Ph_4. A second route to $P(CH_2CMe_3)Ph_2$ involves the reaction between $In(CH_2CMe_3)_3$ and $ClPPh_2$ (eq 7), two species likely to be present in the reaction mixture. However, the indium product from this reaction (eq 7), $In(CH_2CMe_3)_2Cl$,[8] was not an observed product from the reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$. Thus, $In(CH_2CMe_3)_2Cl$[8] must have reacted with another species such as $K[(Me_3CCH_2)_3InPPh_2]$ if it was formed at all. Independent experimental observations demonstrated that $In(CH_2CMe_3)_2Cl$ reacts readily with $K[(Me_3CCH_2)_3InPPh_2]$ to form $In(CH_2CMe_3)_3$, $(Me_3CCH_2)_2InPPh_2$, and KCl (eq 8). Trisneopentylindium reacts, in turn, with $P(CH_2CMe_3)Ph_2$ to form the observed adduct (eq 9). The availability of two different paths to $P(CH_2CMe_3)Ph_2$ (eqs 6 and 7) permits all intermediates to be consumed but only two indium phosphorus products to be isolated at the end of the reaction. The overall reaction is summarized by eq 10.

The series of equations shown by eq 3−9 accounts for all products from the reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$. The initial reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ (eq 3) and the hydrocarbon elimination reaction (eq 4) are slower than the reactions depicted by eqs 5, 6, 7, 8, and 9. The apparent slowness of the replacement of the chlorine on phosphorus by the hydridic hydrogen on indium and the even slower elimination reaction between $In(CH_2CMe_3)_3$ and $HPPh_2$ provide the opportunity for the occurrence of reactions not observed for the $KIn(CH_2CMe_3)_3H$ and $ClP(t\text{-}Bu)_2$ system.[7]

Experimental Section

All compounds were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting materials KH and $ClPPh_2$ were purchased from Aldrich Chemical Co., $HPPh_2$ was purchased from Strem Chemicals, Inc., and $In(CH_2CMe_3)_3$[9] and $KIn(CH_2CMe_3)_3H$[6] were prepared by using literature methods. All solvents were dried by conventional procedures. The ^1H NMR spectra were recorded at 400 MHz by using a Varian Unity-Inova 400 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to $SiMe_4$ at δ 0.00 ppm and benzene at δ 7.15 ppm. The ^{31}P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectra of solids were observed as Nujol mulls between KBr plates and were recorded with a Perkin-Elmer 683 spectrometer. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with purified argon and are uncorrected.

Synthesis of $(Me_3CCH_2)_2InPPh_2$ from $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$. (a) Mixing Reagents at −45 °C in Pentane. A tube, charged with 0.881 g (2.39 mmol) of $KIn(CH_2CMe_3)_3H$ and 10 mL of pentane, was connected to a two-necked flask that contained 0.529 g (2.40 mmol) of $ClPPh_2$ and 20 mL of pentane. The solution of $ClPPh_2$ was cooled to −45 °C with a 2-propanol/dry ice bath, and then the reagents were combined. The resulting mixture was slowly warmed to room temperature and stirred for 2 days. The noncondensable gas H_2 (0.667 mmol, 55.8% based on $KIn(CH_2CMe_3)_3H$, see Results and

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Discussion) was measured with a Toepler pump-gas buret assembly while the solution was maintained at −196 °C. Then the product mixture was warmed to room temperature and filtered with a medium glass frit, and the pentane was removed by vacuum distillation. The insoluble solid (KCl) was isolated and weighed in the drybox (0.168 g, 2.25 mmol, 94.1% yield based on $KIn(CH_2CMe_3)_3H$). The pentane-soluble solid was transferred to a sublimator, whereupon the adduct $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$ (0.476 g, 0.815 mmol, 34.1% yield based on $KIn(CH_2CMe_3)_3H$) sublimed at 90−115 °C. The residue was impure $(Me_3CCH_2)_2InPPh_2$ (0.566 g, 1.29 mmol, 54.0% yield based on $KIn(CH_2CMe_3)_3H$). The organoindium phosphide was purified by recrystallization from 20 mL of pentane at −30 °C to yield 0.301 g (0.681 mmol) in the first crop of cystals and then 0.265 g (0.598 mmol) in the second. Thus, the total yield of $(Me_3CCH_2)_2InPPh_2$ was 0.566 g (1.28 mmol, 53.5% yield based on $KIn(CH_2CMe_3)_3H$).

$(Me_3CCH_2)_2InPPh_2$: mp 143−150 °C dec (lit.[2,3] 143−150 °C dec); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −49.7 (s, $[(Me_3CCH_2)_2InPPh_2]_2$), −30.2 (s, $(Me_3CCH_2)_2InPPh_2$) (lit.[2,3] −49.40, −29.95); ^1H NMR (C_6D_6) δ 1.00 (s, CMe_3, 1 H), 1.06 (s, CMe_3, 18 H), 1.46 (br, $PInCH_2$, 4 H) (lit.[2,3] 1.03, 1.10, 1.47 (t)).

$(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$: mp 82−84 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.1 (s, $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$); ^1H NMR (C_6D_6) δ 0.96 (s, $PCCMe_3$, 9 H), 1.09 (s, $InCH_2$, 6 H), 1.14 (s, $InCCMe_3$, 27 H), 2.07 (d, PCH_2, $J = 4$ Hz, 2 H).

(b) Mixing Reagents at 0 °C in Benzene. The reagents $KIn(CH_2CMe_3)_3H$ (1.39 g, 3.78 mmol) and $ClPPh_2$ (0.835 g, 3.78 mmol) were combined as described previously for pentane but by using benzene at an initial reaction temperature of 0 °C. The isolated products included H_2 (1.32 mmol, 69.8% yield based on $KIn(CH_2CMe_3)_3H$), CMe_4 (separated by vacuum fractional distillation through two −78 °C traps into a −196 °C trap, 0.0735 g, 1.02 mmol, 27.0% yield based on $KIn(CH_2CMe_3)_3H$), KCl (0.252 g, 3.39 mmol, 89.7% yield based on $KIn(CH_2CMe_3)_3H$), $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$ (0.784 g, 1.34 mmol, 35.4% yield based on $KIn(CH_2CMe_3)_3H$), and $(Me_3CCH_2)_2InPPh_2$ (0.674 g, 1.52 mmol, 40.2% yield based on $KIn(CH_2CMe_3)_3H$). The characterization data (mp, ^{31}P and ^1H NMR spectra) for the two indium−phosphorus products were identical to data given previously.

Synthesis of $P(CH_2CMe_3)Ph_2$. The Lewis base $P(CH_2CMe_3)Ph_2$ was synthesized from $ClPPh_2$ (10.2 g, 46.1 mmol) and $(Me_3CCH_2)MgCl$ (61.6 mmol) at 0 °C as described in the literature.[8] The phosphine (7.91 g, 30.9 mmol, 67.0% yield based on $ClPPh_2$) was isolated as a colorless liquid by vacuum distillation (10^{-3} mm) at an oil bath temperature of 100−110 °C and a head temperature of 70−74 °C. Additional drying of the phosphine with $MgSO_4$ followed by short-path vacuum distillation at a head temperature of 84−94 °C and 10^{-3} mm pressure (bp lit.[8] 110−111 °C, 0.2 mm) gave the pure phosphine: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.1 (lit.[8] −23.3); ^1H NMR (C_6D_6) δ 0.99 (s, $PCCMe_3$, 9 H), 2.07 (d, PCH_2, $J = 5$ Hz, 2 H), 7.04 (td, Ph, $J = 11$ Hz, 10 H), 7.45 (dd, Ph, $J = 10$ Hz, 10 H) (lit.[8] $CDCl_3$: 1.00, 2.15, 7.13−7.62).

Synthesis and NMR Spectra of $(Me_3CCH_2)_3In{\cdot}P(CH_2CMe_3)Ph_2$. An NMR tube was charged with $P(CH_2CMe_3)Ph_2$ (0.124 g, 0.482 mmol), $In(CH_2CMe_3)_3$ (0.159 g, 0.483 mmol), and C_6D_6. The walls of the tube were carefully rinsed with the benzene to ensure complete mixing of the reagents. Then after the tube was flame sealed under vacuum, the NMR spectrum was recorded immediately. $^{31}P\{^1H\}$ NMR (C_6D_6) δ: −22.8. ^1H NMR (C_6D_6) δ: 0.90 (s, $PCCMe_3$, 9 H), 1.16 (s, $InCH_2$, 6 H), 1.19 (s, $InCCMe_3$, 27 H), 2.08 (d, PCH_2, $J = 5$ Hz, 2 H).

Reaction of $KIn(CH_2CMe_3)_3H$ with $HPPh_2$. A pentane solution of $HPPh_2$ (0.403 g, 2.16 mmol) was added to a pentane solution of $KIn(CH_2CMe_3)_3H$ (0.802 g, 2.18 mmol) that had been cooled to −50 to −60 °C. Bubbling, formation of a precipitate, and a color change from colorless to light yellow were observed upon mixing the reagents. After the solution had been warmed to room temperature and stirred for 18 h, the noncondensable gas (H_2) was measured at −196 °C with a Toepler pump-gas buret assembly (1.40 mmol H_2, 64.8% H_2 based on $HPPh_2$).

NMR Spectral Study of Reaction Products after Mixing $In(CH_2CMe_3)_3$ with $ClPPh_2$. A small tube was charged with $ClPPh_2$ (0.182 g, 0.826 mmol), $In(CH_2CMe_3)_3$ (0.271 g, 0.827 mmol), and C_6D_6 (1 mL). Then, a portion of the contents was transferred to an NMR tube under vacuum and the NMR tube was flame-sealed. The NMR spectrum was recorded 30 min after mixing of reagents. The products identified by the NMR spectrum included $In(CH_2CMe_3)_2Cl$ and $P(CH_2CMe_3)Ph_2$. $^{31}P\{^1H\}$ NMR (C_6D_6) δ: −41.0 (d, $J = 310$ Hz, trace $HPPh_2$), −21.1 (s, $P(CH_2CMe_3)Ph_2$), −21.2 (d, $J = 310$ Hz, trace). ^{31}P NMR (C_6D_6) δ: −41.2 (d, $J = 314$ Hz, trace), −21.1 (s, $P(CH_2CMe_3)Ph_2$), −21.2 (d, $J = 310$ Hz, trace). ^1H NMR (C_6D_6) δ: 0.86 (br, 0.8 H), 0.90 (s, 0.4 H), 0.94 (br, $PCCMe_3$, 7.4 H), 1.17 (s, $InCCMe_3$, 18 H), 1.27 (br, 1.3. H), 1.30 (s, 4.3 H), 1.56 (s, $InCH_2$, 4 H), 7.09 (d, PPh, $J = 6$ Hz, 5.3 H), 7.38 (br, 0.4 H), 7.43 (td, PPh, $J = 8$ Hz, 3.2 H).

Synthetic Scale Reaction between $In(CH_2CMe_3)_3$ and $ClPPh_2$. A pentane (5 mL) solution of $ClPPh_2$ (0.980 g, 4.44 mmol) was added to a pentane (15 mL) solution of $In(CH_2CMe_3)_3$ (1.46 g, 4.44 mmol) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. Pentane was removed by vacuum distillation while holding the product mixture at −30 °C. Then $In(CH_2CMe_3)_2Cl$ was crystallized from fresh pentane at −20 to −30 °C and isolated by filtration. After the pentane was removed by vacuum distillation with the flask held in an ice bath, 0.966 g of $In(CH_2CMe_3)_2Cl$ (3.30 mmol, 74.3% yield based on $ClPPh_2$) and a cloudy viscous liquid were obtained. The cloudy liquid was purified by vacuum distillation with a short-path still by using an oil bath at 105 °C. The phosphine $P(CH_2CMe_3)Ph_2$ (0.827 g, 3.23 mmol, 72.7% based on $ClPPh_2$) distilled at a head temperature of 78 °C.

$In(CH_2CMe_3)_2Cl$: ^1H NMR (C_6D_6) δ 1.09 (s, $InCCMe_3$, 9 H), 1.58 (s,$InCH_2$, 2 H) (lit.[6] 1.09, 1.58).

$P(CH_2CMe_3)Ph_2$: ^1H NMR (C_6D_6) δ 1.01 (s, PCH_2, 9 H), 1.13 (s, $InCCMe_3$, ~1 H), 1.51 (s, $InCH_2$, ~0.2 H), 2.09 (d, PCH_2C, $J = 4$ Hz, 2 H), 7.08 (m, p, m-H of PPh, 6 H), 7.47 (t, o-H of PPh, 4H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −21.4 (s, $P(CH_2CMe_3)Ph_2$); ^{31}P NMR (C_6D_6) δ −21.4 (br, $P(CH_2CMe_3)Ph_2$).

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